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Syntheses of Charge-Compensated Dicarbollide Ligand Precursors and Their Use in the Preparation of Novel Metallacarboranes

by
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A series of charge-compensated, boron-substituted carborane cage derivatives, [*nido*-9-L-7,8-$C_2B_9H_{11}$] or [*nido*-10-L-7,8-$C_2B_9H_{11}$] (L = nitrogen-containing ligand), were prepared by the ferric chloride-promoted oxidative coupling reaction of K[*nido*-7,8-$C_2B_9H_{12}$] with the Lewis base, L. Another series of neutral boron-substituted carborane cage derivatives, [*nido*-10-L-7,9-$C_2B_9H_{11}$], were synthesized directly from the reaction of [*closo*-1,8-$C_2B_9H_{11}$] with the nitrogen-containing ligand, L. When Na[*nido*-10-N-$(C_2H_5)_3$-7,8-$C_2B_9H_{10}$] (Na-2), Na[*nido*-9-(4-$(C_5H_4N)CO_2CH_3$)-7,8-$C_2B_9H_{10}$] (Na-3), or Na[*nido*-10-C_5H_5N-7,9-$C_2B_9H_{10}$] (Na-4) were reacted with anhydrous ferrous chloride in THF at 298 K, the three corresponding ferrocene-like neutral *commo*-ferracarboranes were obtained. The complex [*commo*-3,3'-Fe[8-$N(C_2H_5)_3$-3,1,2-$FeC_2B_9H_{10}]_2$] (5) was characterized both by spectroscopic methods and by a single-crystal X-ray diffraction study. The well-known unsubstituted iron sandwich [*commo*-3,3'-Fe[3,1,2-$FeC_2B_9H_{11}]_2$][$N(CH_3)_4]_2$ (6) was also characterized crystallographically for the first time. Complexes 5 and 6 each crystallized in the monoclinic space group $P2_1/c$, with a = 9.017 (3) Å, b = 11.341 (3) Å, c = 32.941 (11) Å, β = 91.84 (1)°, V = 3409 Å^3, and Z = 4 for 5 and a = 7.278 (2) Å, b = 15.830 (4) Å, c = 11.994 (3) Å, β = 91.80 (2)°, V = 1381 Å^3, and Z = 2 for 6. The sandwich species [*commo*-3,3'-Fe[4-(4-$(C_5H_4N)CO_2CH_3$)-3,1,2-$FeC_2B_9H_{10}]_2$] (7) and [*commo*-2,2'-Fe[1-C_5H_5N-2,1,7-$FeC_2B_9H_{10}]_2$] (8) were characterized by spectroscopic means. A novel cationic cobaltacarborane sandwich analogous to the cobalticenium ion, [*commo*-3,3'-Co[4-(4-$(C_5H_4N)CO_2CH_3$)-3,1,2-$CoC_2B_9H_{10}]_2$]Cl (9-Cl) was isolated and characterized. This is the first example of a cationic metallacarborane that incorporates the dicarbollide ligand.

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